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(54) Title: WETTABLE SILICONE HYDROGEL COMPOSITIONS AND METHODS FOR THEIR MANUFACTURE (57) Abstract Improved silicone-containing hydrogels are disclosed with enhanced wettability comprising a silicone-containing monomer, at least one acrylic-containing hydrophilic monomer, and at least one vinyl-containing hydrophilic monomer.		

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**WETTABLE SILICONE HYDROGEL COMPOSITIONS
AND METHODS FOR THEIR MANUFACTURE**

BACKGROUND OF THE INVENTION

This application is a continuation-in-part application of copending application Ser. No. 07/788,013 filed November 5, 1991.

Field of the Invention

The present invention relates to improved wettable polymeric hydrogel compositions useful for the production of biomedical devices, especially contact lenses.

Background

Hydrogels have been a desirable class of material for the preparation of biomedical devices, and have been known since at least Wichterle, et al U.S. Patent No. 3,220,960 which disclosed hydrogels comprising a hydrated polymer of a hydroxyalkyl acrylate or methacrylate crosslinked with a corresponding diester (poly 2-hydroxyethyl methacrylate, known as poly-HEMA).

A hydrogel is a hydrated crosslinked polymeric system that contains water in an equilibrium state. The physical properties of hydrogels can vary widely and are mostly determined by their water content. Since hydrogels exhibit excellent biocompatibility, there has

been extensive interest in the use of hydrogels for biomedical devices, especially contact lenses.

In the field of contact lenses, various factors must combine to yield a material that has appropriate characteristics. Oxygen permeability, wettability, material strength and stability are but a few of the factors which must be carefully balanced to achieve a useable end-result contact lens. Since the cornea receives its oxygen supply exclusively from contact with the atmosphere, good oxygen permeability is a critical characteristic for any contact lens material.

It was discovered that certain crosslinked polymeric materials could be hydrated and retain their water content. It was further found that the higher the water content within contact lenses made from these crosslinked hydrogel polymers, the greater was the oxygen permeability through the lens to the cornea.

High water-containing hydrogels have at times exhibited undesirable mechanical properties. For example, such hydrogels are often not easily formed into hydrolytically stable lenses. Further such materials have at times exhibited tearing or other breakage as a result of poor tensile strength. What was needed was a highly oxygen permeable material that was durable and

highly wettable. Wettability is important in that, if the lens is not sufficiently wettable, it does not remain lubricated and therefore cannot be worn comfortably in the eye. The optimum contact lens would have not only excellent oxygen permeability, but also excellent tear fluid wettability.

Silicone-containing materials were tried as viable contact lens materials and displayed very good oxygen permeability and durability. However, most silicone-containing materials are largely hydrophobic and therefore not sufficiently wettable. Further, it is believed that such hydrophobicity causes enhanced deposit problems, which may also result in discomfort when wearing contact lenses made from certain silicone-containing polymers.

Therefore, an optimal hydrogel material for biomedical devices, such as contact lenses, would have ideal rigidity, high oxygen permeability and a high degree of wettability.

SUMMARY OF THE INVENTION

In accordance with this invention, the surface wettability of hydrogels, such as silicone-containing

hydrogels, and more specifically polyurethane-silicone hydrogels and ethylenically terminated polysiloxane hydrogels such as (poly)organosiloxane hydrogels, are significantly enhanced by incorporating both at least one vinyl-containing hydrophilic monomer and at least one acrylic-containing hydrophilic monomer into the monomer mix along with the silicone-containing monomer or prepolymer.

Further, in accordance with the present invention, a method for making a wettable silicone-containing hydrogel composition is disclosed comprising the steps of a) combining at least one vinyl-containing monomer, at least one acrylic-containing monomer and at least one silicone-containing monomer or prepolymer into a monomer mix and b) curing the monomer mix resulting from step a) to form a silicone-containing hydrogel composition.

It is believed that the combined vinyl-containing and acrylic-containing monomers act as wetting agents, and interact with the predominantly hydrophobic silicone-containing monomers and prepolymers in the monomer mix to produce highly wettable hydrogels with ideal rigidity. Such resultant hydrogels are especially well-suited for use as contact lens materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 depict the effect on modulus of polyurethane films as the composition ratio of NVP to DMA is changed.

Figure 3 depicts the effect on modulus of methacrylate-capped polysiloxane films as the composition ratio of NVP to DMA is changed.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to improved wettability of hydrogels, especially silicone-containing hydrogels with ideal rigidity suitable for biomedical applications such as contact lenses.

The silicone-containing hydrogels of the present invention display improved wettability as a result of the combined presence in the monomer mix of at least one acrylic-containing monomer and at least one vinyl-containing monomer.

Silicone hydrogels (i.e., hydrogels containing silicone) are usually prepared by polymerizing a mixture containing at least one silicone-containing monomer and

at least one hydrophilic monomer. Either the silicone-containing monomer or the hydrophilic monomer may function as a crosslinking agent (a crosslinker being defined as a monomer having multiple polymerizable functionalities) or a separate crosslinker may be employed.

The term "vinyl-containing" is meant to refer to non-acrylic monomers having the vinyl grouping ($\text{CH}_2=\text{CH}-$) which are generally highly reactive. Such vinyl groups are known to polymerize relatively easily. "Acrylic-containing" monomers are those compounds containing the acrylic grouping ($\text{CH}_2=\text{C}(\text{R})\text{COX}$) which are also generally reactive.

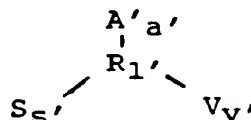
The vinyl-containing monomers used in the present invention include hydrophilic monomers such as N-vinyl pyrrolidone, N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-methyl formamide, N-vinyl formamide, with N-vinyl pyrrolidone (NVP) being the most preferred.

The acrylic-containing monomers used in the present invention include hydrophilic monomers such as 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxyethyl methacrylamide, N,N-dimethyl (meth)acrylamide, diacetone acrylamide, methacrylic acid

and acrylic acid with N,N-dimethylacrylamide (DMA) being the most preferred.

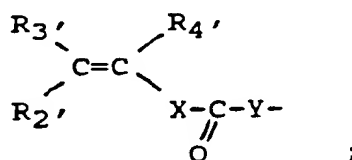
When both vinyl- and acrylic-containing monomers are present within one monomer mixture, it is preferable to add a crosslinking composition containing at least one vinyl-containing polymerizable group and at least one acrylic- or styrene-containing polymerizable group disclosed in copending and commonly assigned U.S. Application No. 07/788,071 filed November 5, 1991 and having the following general schematic representation (I):

(I)

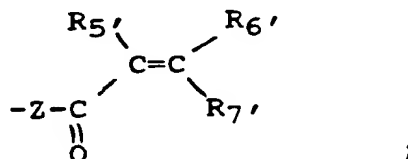


wherein:

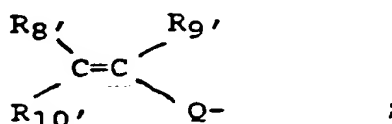
V denotes



A' denotes

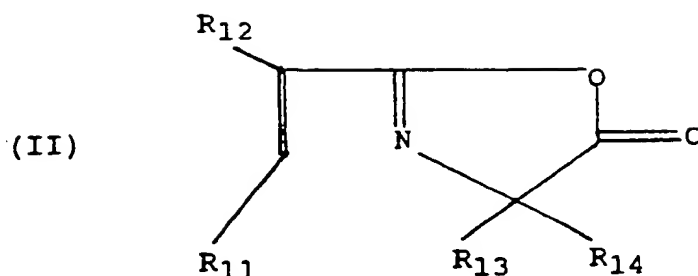


S denotes



- R_1' is an alkyl radical derived from substituted and unsubstituted hydrocarbons, polyalkylene oxide, poly(perfluoro) alkylene oxide, dialkyl-capped polydimethylsiloxane, dialkyl-capped polydimethylsiloxane modified with fluoroalkyl or fluoroether groups;
- $R_2', -R_{10}'$ are independently H, or alkyl of 1 to 5 carbon atoms;
- Q is an organic group containing aromatic moieties having 6 to 30 carbon atoms;
- X, Y, and Z are independently O, NH or S;
- v' is 1, or higher; and
- a', s' independently are greater than or equal to 0, and $a' + s' \geq 1$.

The addition of crosslinking agents of Formula I assists in the copolymerization of the vinyl-and acrylic-containing monomers with each other as well as with other monomers and prepolymers present in the monomer mix, such as the relatively non-polar ring-containing oxazolone compounds of the general formula (II):



where

R_{11} and R_{12} independently denote H or CH_3 ; and
 R_{13} and R_{14} independently denote methyl or
 cyclohexyl radicals.

These ring-containing monomers which may be incorporated into the silicone-containing hydrogels of the present invention specifically include 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (IPDMO), 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (VDMO), cyclohexane spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one) (IPCO), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) (VCO), and 2-(-1-propenyl)-4,4-dimethyl-oxazol-5-one (PDMO). The preferred oxazolones are prepared by known reaction sequences set forth in commonly assigned U.S. Patent No. 4,810,764. The amount of crosslinker used is about 0.01 to about 5% of the vinyl-containing monomer weight present in a useful formulation.

We have observed that silicone-containing hydrogels containing NVP as a wetting agent have a much higher

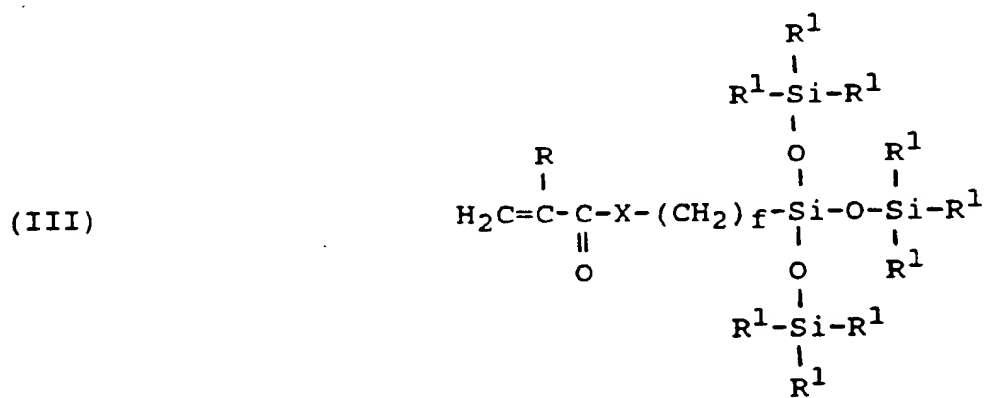
modulus as compared with silicone hydrogels that incorporate acrylic-containing monomers, such as glycerol methacrylate and, N,N-dimethylacrylamide (DMA). We observed, and this invention contemplates, that the incorporation of a vinyl-containing hydrophilic monomer with an acrylic-containing hydrophilic monomer as wetting agents into silicone-containing formulations results in hydrogels suitable for biomedical applications, especially contact lenses.

Any known silicone-containing prepolymer may be used to form the silicone hydrogels of this invention, as will be apparent to one skilled in the art. The monomers added to the monomeric mixture may be monomers or prepolymers. A "prepolymer" is a reaction intermediate polymer of medium molecular weight having polymerizable groups. Thus it is understood that the terms "silicone-containing monomers" and "hydrophilic monomers" include prepolymers. Examples of such monomers may be found in United States Patent Nos. 4,136,250; 4,153,641; 4,740,533; 5,034,461; and 5,070,215.

Further, notations such as "(meth)acrylate or "(meth)acrylamide are used herein to denote optional methyl substitution. Thus, for example, methyl (meth)acrylate includes both methyl acrylate and methyl

methacrylate and N-alkyl (meth)acrylamide includes both N-alkyl acrylamide and N-alkyl methacrylamide.

One preferred class of suitable silicone-containing monomers are bulky polysiloxanylalkyl (meth)acrylic monomers represented by the formula (III):



wherein:

X is O or NR;

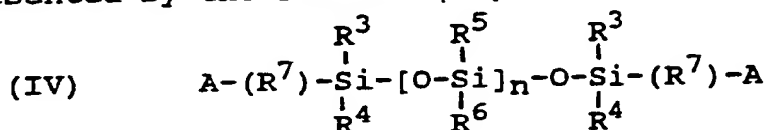
each R is independently hydrogen or methyl; and

each R¹ is independently a lower alkyl or phenyl group; and

f is 1 or 3 to 10.

Such bulky monomers include methacryloxypropyl tris(trimethylsiloxy)silane, pentamethyldisiloxanylmethylmethacrylate, tris(trimethylsiloxy)methacryloxy propylsilane, phenyltetramethyldisiloxanylethyl acetate, and methyldi(trimethylsiloxy)methacryloxymethyl silane.

A further preferred class of silicone-containing monomers are the poly(organosiloxane) prepolymers represented by the formula (IV):



wherein:

A is an activated unsaturated group, such as an ester or amide of an acrylic or a methacrylic acid;

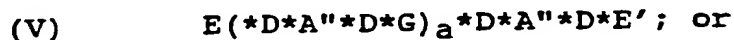
each R^3 - R^6 is independently selected from the group consisting of a monovalent hydrocarbon radical or a halogen substituted monovalent hydrocarbon radical having 1 to 18 carbon atoms which may have ether linkages between carbon atoms;

R^7 is a divalent hydrocarbon radical having from 1 to 22 carbon atoms;

and

n is 0 or an integer greater than or equal to 1.

A further preferred class of silicone-containing monomers are the monomers having the following schematic representations:



where

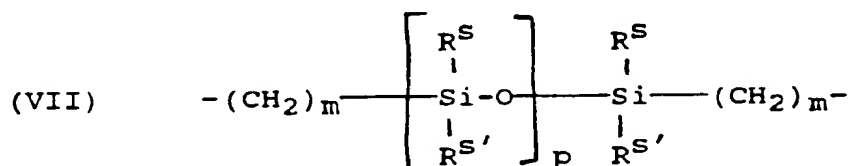
D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 1 to 40 carbon atoms and which may contain ether, thio or amine linkages in the main chain;

* denotes a urethane or ureido linkage;

a is at least 1;

A" denotes a divalent polymeric radical of formula (VII):

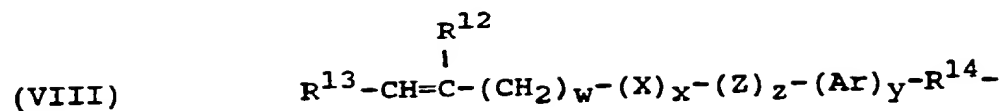


wherein: R^{S} and $\text{R}^{\text{S}'}$ independently denote an alkyl or fluoro-substituted alkyl group having 1 to 10 carbon atoms which may contain ether linkages between carbon atoms;

m is at least 1; and

p provides a moiety weight of 400 to 10,000;

E and E' independently denote a polymerizable unsaturated organic radical represented by formula (VIII):



wherein: R^{14} denotes a divalent alkylene radical having 1 to 10 carbon atoms;

R^{12} denotes H or CH_3 ;

R^{13} denotes H, a (C_1 - C_6) alkyl radical or a $-CO-Y-R^{15}$ group wherein Y is $-O-$, $-S-$ or $-NH-$ and R^{15} is a alkyl radical having 1 to 12 carbon atoms;

X is $-CO-$ or $-OCO-$;

Z is $-O-$ or $-NH-$;

Ar denotes an aromatic radical having 6 to 30 carbon atoms;

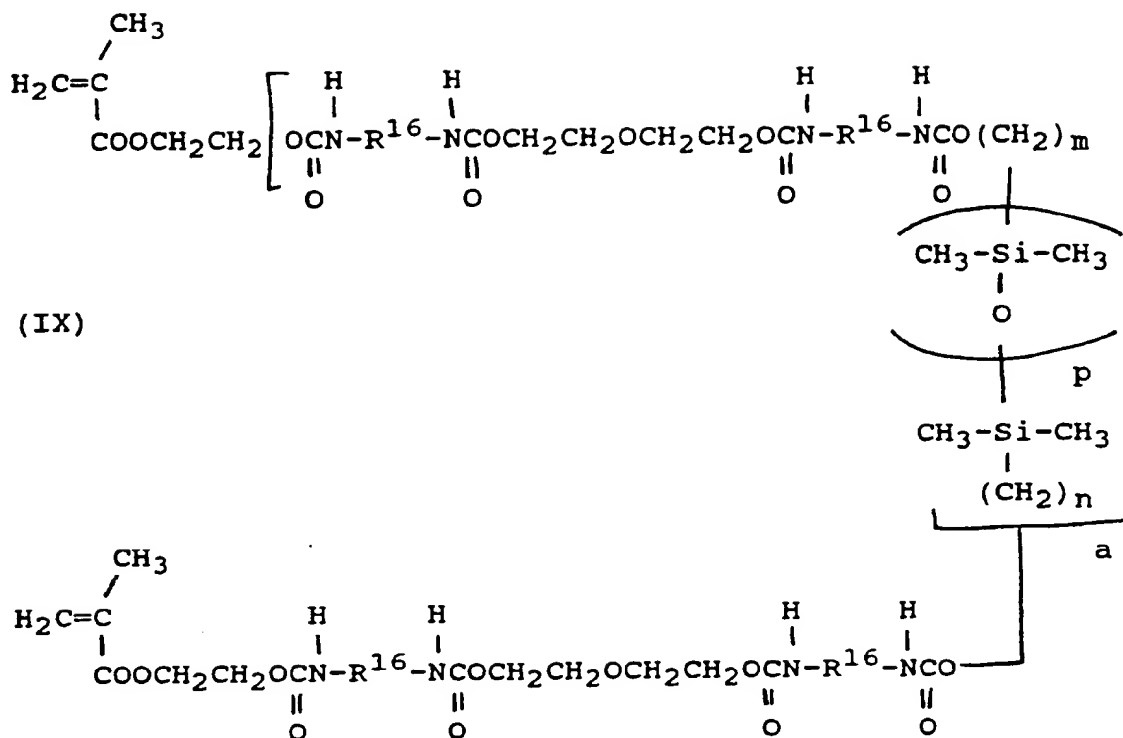
w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

z is 0 or 1.

A preferred urethane monomer is represented by formula (IX):



wherein:

R^{16} is a diradical of a diisocyanate after removal of the isocyanate group, and is most preferably the diradical of isophorone diisocyanate, and m , p and a are the same as previously defined. Preferably, the sum of m and a is 3 or 4, and more preferably, a is 1 and m is 3 or 4. Preferably, p is at least 30.

The wettable silicone-containing hydrogels of the present invention, when used in contact lens applications, can produce a wide variety of types of hydrogel contact lenses. As is understood in the field, in general, hydrogel contact lenses should have oxygen

permeabilities with DK values greater than about $20 \times 10^{-11} \text{ cm}^3 \times \text{cm/sec} \times \text{cm}^2 \times \text{mmHg}$ (or 20 DK units) and preferably greater than about 60 DK. They should have a Young's modulus of elasticity in the range of about 5 to 400 g/mm^2 , preferably greater than about 20 g/mm^2 as measured by ASTM test method D1938. Their water content should be between about 10 and 80 %, and preferably between 20 and 60%. The contact angle, which is a measurement of the wettability of the lens, should be less than about 80 degrees and should preferably be less than about 40 degrees.

The preferred range of the combined vinyl-containing and acrylic-containing hydrophilic wetting monomer concentration is from about 5 weight percent of the polymeric hydrogel mix to about 80 weight percent, and more preferably from about 20 weight percent to about 60 weight percent. The weight ratio of vinyl-containing monomer to acrylic-containing monomer is from about 40:1 to about 1:40, and is preferably higher than 1:1.

The present invention further provides articles of manufacture which can be used for biomedical devices, such as, contact lenses, surgical devices, heart valves, vessel substitutes, intrauterine devices, membranes and other films, diaphragms, surgical implants, blood

vessels, artificial ureters, artificial breast tissue and membranes intended to come into contact with body fluid outside of the body, e.g., membranes for kidney dialysis and heart/lung machines and the like, catheters, mouth guards, denture liners, intraocular devices, and especially contact lenses.

It is known that blood, for example, is readily and rapidly damaged when it comes into contact with artificial surfaces. The design of a synthetic surface which is antithrombogenic and nonhemolytic to blood is necessary for prostheses and devices used with blood.

The terms "shaped articles for use in biomedical applications" or "biomedical devices" mean the materials disclosed herein have physicochemical properties rendering them suitable for prolonged contact with living tissue, blood and the mucous membranes.

Although the exact mechanisms are not fully understood at the present time, the wetting agents of the present invention appear to reduce the deposition problems normally associated with, and believed to be caused by, the high hydrophobicity of the hydrophobic silicone-containing monomers.

Further, the wetting agents of the present invention significantly reduce the contact angle of the surface - a clear indication to those skilled in the field that enhanced wetting has occurred. The resulting novel hydrogels comprising the wetting agents of the present invention were unexpectedly hydrolytically stable, within an acceptable range, while collecting only an acceptable level of deposits.

Two preferred classes of silicone-containing monomers contemplated by the present invention are urethane-containing prepolymers, and ethylenically terminated polysiloxane containing monomers as previously described herein, such as, most preferably α,ω bis(methacryloxyalkyl)polysiloxane.

The resulting polymers and copolymers disclosed herein can be boiled and/or autoclaved in water without being damaged whereby sterilization may be achieved. Thus, an article formed from the disclosed polymers and copolymers may be used, for example, in surgery where an article is needed which is compatible with living tissue or with the mucous membranes.

The monomer mixes employed in this invention, can be readily cured to cast shapes by conventional methods such as UV polymerization, or thermal polymerization, or

combinations thereof, as commonly used in polymerizing ethylenically unsaturated compounds. Representative free radical thermal polymerization initiators are organic peroxides, such as acetal peroxide, lauroyl peroxide, decanoyl peroxide, stearoyl peroxide, benzoyl peroxide, tertiarybutyl peroxyvalate, peroxydicarbonate, and the like, employed in a concentration of about 0.01 to 1 percent by weight of the total monomer mixture. Representative UV initiators are those known in the field such as, benzoin methyl ether, benzoin ethyl ether, Darocure 1173, 1164, 2273, 1116, 2959, 3331 (EM Industries) and Igracure 651 and 184 (Ciba-Geigy).

Polymerization of the monomer mix of this invention may be performed in the presence of a diluent. The polymerization product will then be in the form of a gel. If the diluent is nonaqueous, the diluent must be removed from the gel and replaced with water through the use of extraction and hydration protocols well known to those skilled in the art.

It is also possible to perform the polymerization in the absence of diluent to produce a xerogel. These xerogels may then be hydrated to form the hydrogels as is well known in the art.

In addition to the above-mentioned polymerization initiators, the copolymer of the present invention may also include other monomers as will be apparent to one skilled in the art. For example, the monomer mix may include additional hydrophilic monomers, colorants, curing agents, or UV-absorbing and toughening agents such as those known in the contact lens art.

The polymers of this invention can be formed into contact lenses by spincasting processes (such as those disclosed in U.S. Pat. Nos. 3,408,429 and 3,496,254), cast molding processes (such as those disclosed in U.S. Pat. Nos. 4,084,459 and 4,197,266), combinations of methods thereof, or any other known method for making contact lenses. Polymerization may be conducted either in a spinning mold, or a stationary mold corresponding to a desired contact lens shape. The lens may be further subjected to mechanical finishing, as occasion demands. Polymerization may also be conducted in an appropriate mold or vessel to form buttons, plates or rods, which may then be processed (e.g., cut or polished via lathe or laser) to give a contact lens having a desired shape.

The hydrogels the present invention are oxygen transporting, hydrolytically stable, biologically inert, and transparent. The monomers and prepolymers employed

in accordance with this invention, are readily polymerized to form three dimensional networks which permit the transport of oxygen and are optically clear, strong and hydrophilic.

The relative softness or hardness of the contact lenses fabricated from the resulting polymer of this invention can be varied by decreasing or increasing the molecular weight of the polysiloxane prepolymer end-capped with the activated unsaturated group or by varying the percent of the comonomer. As the ratio of polysiloxane units to end-cap units increases, the softness of the material increases.

The following examples serve only to further illustrate aspects of the present invention and should not be construed as limiting the invention.

The following abbreviations are defined as follows:

NVP	is N-vinyl pyrrolidone
DMA	is N,N-dimethyl acrylamide
HEMAVc	is methacryloxyethyl vinyl carbonate
TRIS	is methacryloxypropyl tris(trimethylsiloxy)silane
IDS3H	is a urethane prepolymer derived from isophorone diisocyanate, diethylene

glycol, polysiloxanediol encapped with 2-hydroxyethyl methacrylate

M₂D_x is an α,ω -bis(methacryloxyalkyl)-polysiloxane

VDMO is 2-vinyl-4,4-dimethyl-2-oxazoline-5-one

EXAMPLES 1-6

Polyurethane-silicone Hydrogels

Six polyurethane hydrogel films containing the following ingredients, were prepared:

- a) IDS3H, 30 parts;
- b) TRIS, 30 parts;
- c) NVP, varied from 0 to 40 parts;
- d) DMA, varied from 40 to 0 parts (NVP + DMA = 40 parts)
- e) Methacryloxyethylvinyl carbonate (HEMAVc crosslinker) at 0.3% of NVP amount;
- f) n-Hexanol 40 parts;
- g) Darocur-1173, (UV initiator), 0.2 part.

These formulations were UV cured, followed by ethanol extraction and boiling water hydration, as is known in the art, to give resultant hydrogel films with the following properties (water content and modulus). Figure 1 depicts the resultant films of Examples 1-6 with one plotted point for each film respectively.

Table 1

EXAMPLE	1	2	3	4	5	6
NVP/DMA ratio	40/0	38/2	35/5	30/10	20/20	0/40
% water	35	46	44	41	41	37
Modulus	430	281	150	80	79	63

The modulus/composition relationship is depicted in Figure 1.

EXAMPLE 7

Polyurethane Hydrogel

A formulation was prepared containing the same ingredients and same weight ratios as those in Example 4, except that 3 parts of NVP and 1 part of DMA was replaced by 1 part of VDMO. The formulation was cast onto films and processed as done in Examples 1-6. The resulting hydrogel films had the following properties: water content, 40%; modulus 110 g/mm².

EXAMPLES 8-11

Polyurethane-silicone Hydrogels

Polyurethane formulations of the ingredients as in Examples 1-6 but of different relative parts, as shown in Table 2, were prepared.

- a) IDS3H & b) TRIS, 34 parts each;
c) NVP & d) DMA, 32 parts combined;
e) n-Hexanol, f) HEMAvc and g) Darocure-1173, same parts as in Examples 1-6.

The formulations were cast and processed in the same manner as in Examples 1-6, with the water content and modulus data shown in Table 2. Figure 2 depicts the resultant films of Examples 8-11, with one plotted point representing each film respectively.

Table 2				
EXAMPLE	8	9	10	11
NVP/DMA ratio	32/0	24/8	16/16	0/32
water %	25	26	31	25
Modulus	610	275	107	87

The modulus/composition relationship is further shown in Figure 2.

EXAMPLES 12-15

M₂D_x-based Hydrogel Films

The following silicone hydrogel formulations were prepared and cast processed into hydrogel films by the procedure of Examples 8-11. Figure 3 depicts the resultant films of Examples 8-11, with one plotted point representing each film respectively. The ingredients in the formulation were:

- a) M_2D_x , 13 parts
- b) TRIS, 47 parts
- c) NVP & d) DMA, 40 parts combined
- e) n-Hexanol, 40 parts
- f) HEMAvc, 0.3 part of NVP amount
- g) Darocur, 0.2 part

The modulus-composition relationship is depicted in Figure 3.

EXAMPLE 16

Hydrogel Lens Casting

A monomer mix of the formulation as described in Examples 4, 9, 12 was filtered through a disposable 1.2 micron millipore filter into a clean vial. Under an inert nitrogen atmosphere, 60-90 ul of the mix was injected onto a clean plastic mold half and then covered with a second plastic mold half. The molds were then compressed and cured for 90 minutes in the presence of UV light (4200 microwatts/cm²). The molds were then opened mechanically and put into a beaker containing aqueous ethanol. The lenses were released from the molds within 1 hour, then extracted with ethanol for 48 hours, and boiled in distilled water for 4 hours. The resultant lenses were inspected for cosmetic quality, cytotoxicity and dimensions. Lenses passing inspection

were thermally disinfected in phosphate buffered saline prior to on-eye evaluation.

EXAMPLE 17

Clinical Evaluations

The cast-molded polyurethane lenses described in Example 12 were evaluated on six to ten patients. In each test, a poly(HEMA) control lens was worn on one eye and the test lens on the other eye. The lenses were analyzed after a minimum of one hour, and preferably 5 hours or longer for wettability and surface deposition study. The surface wettability rating scale was 0-4 with 0 representing 2/3 of the anterior surface unwetted by the tear film, and 4 representing complete wetting. The deposition scale was also 0-4 with 0 representing no surface deposits and 4 representing multiple deposits of 0.5 mm diameter or larger. The results for the lenses of the control formulation (according to Example 4) was 3.0 for wetting and 0.4 for deposits after five hours of wear. For lenses comprising 1 part of VDMO (Example 7 formulation), the results showed a wettability rating of 3.3 and a deposit rating of 0.7 after 5 hours or wear.

Many other modifications and variations of the present invention are possible to the skilled practitioner in the field in light of the teachings herein. It is therefore understood that, within the

scope of the claims, the present invention can be practiced other than as herein specifically described.

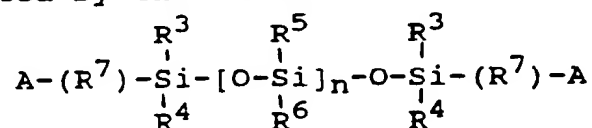
We Claim:

1. A method for making a silicone-containing hydrogel composition comprising the steps of a) combining at least one vinyl-containing monomer, at least one acrylic-containing monomer and at least one silicone-containing prepolymer into a monomer mix and b) curing the monomer mix resulting from step a) to form a silicone-containing hydrogel composition.
2. The method of Claim 1 wherein said silicone-containing prepolymer is a urethane-containing prepolymer.
3. The method of Claim 1 wherein said silicone-containing prepolymer is an ethylenically terminated polysiloxane-containing prepolymer.
4. The method of Claim 1 wherein said vinyl-containing monomer may be selected from the group consisting of: N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-methyl formamide, and N-vinyl formamide.
5. The method of Claim 1 wherein said vinyl-containing monomer is N-vinyl pyrrolidone.
6. The method of Claim 1 wherein said acrylic-containing monomer is selected from the group consisting

of: 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxyethyl methacrylamide, diacetone acrylamide, methacrylic acid and acrylic acid.

7. The method of Claim 1 wherein said acrylic-containing monomer is N,N-dimethylacrylamide.

8. The method of Claim 1 wherein said silicone-containing prepolymer is a poly(organosiloxane) prepolymer represented by the formula:



wherein:

A is an activated unsaturated group, such as an ester or amide of an acrylic or a methacrylic acid;

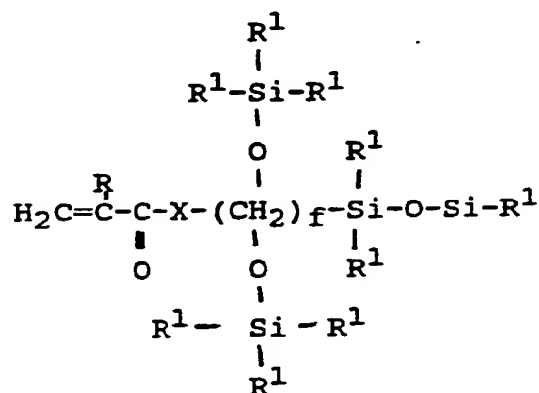
each R^3 - R^6 is independently selected from the group consisting of a monovalent hydrocarbon radical or a halogen substituted monovalent hydrocarbon radical having 1 to 18 carbon atoms which may have ether linkages between carbon atoms;

R^7 is a divalent hydrocarbon radical having from 1 to 22 carbon atoms;

and

n is 0 or an integer greater than or equal to 1.

9. The method of Claim 1 wherein said silicone-containing prepolymer is a bulky polysiloxanyalkyl (meth)acrylic monomer having the formula:



wherein:

X is O or NR;

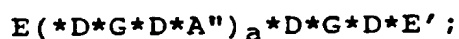
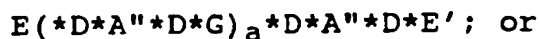
each R is independently hydrogen or methyl; and

each R¹ is independently a lower alkyl or phenyl group; and

f is 1 or 3 to 10.

10. The method of Claim 9 wherein said bulky polysiloxanyalkyl (meth)acrylate monomer is selected from the group consisting of methacryloxypropyl tris(trimethylsiloxy)silane, pentamethyldisiloxanylmethylmethacrylate, tris(trimethylsiloxy)methacryloxy propylsilane, phenyltetramethyldisiloxanylethyl acetate, and methyldi(trimethylsiloxy)methacryloxymethyl silane.

11. The method of Claim 1 wherein said silicone-containing prepolymer is a urethane-containing prepolymer having the following schematic representations:



wherein

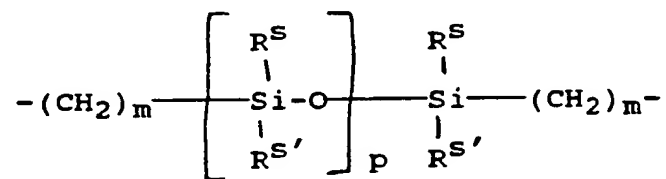
D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 1 to 40 carbon atoms and which may contain ether, thio or amine linkages in the main chain;

* denotes a urethane or ureido linkage;

a is at least 1;

A" denotes a divalent polymeric radical of formula:



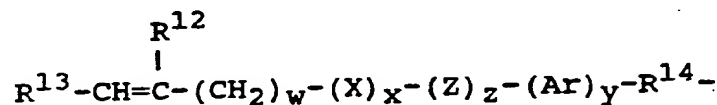
wherein: R^S and $R^{S'}$ independently denote an alkyl or fluoro-substituted alkyl group having 1 to 10 carbon

atoms which may contain ether linkages between carbon atoms;

m is at least 1; and

p provides a moiety weight of 400 to 10,000;

E and E' independently denote a polymerizable unsaturated organic radical represented by formula:



wherein: R^{14} denotes a divalent alkylene radical having 1 to 10 carbon atoms;

R^{12} denotes H or CH_3 ;

R^{13} denotes H, a (C_1-C_6) alkyl radical or a $-CO-Y-R^{15}$ group wherein Y is $-O-$, $-S-$ or $-NH-$ and R^{15} is a alkyl radical having 1 to 12 carbon atoms;

X is $-CO-$ or $-OCO-$;

Z is $-O-$ or $-NH-$;

Ar denotes an aromatic radical having 6 to 30 carbon atoms;

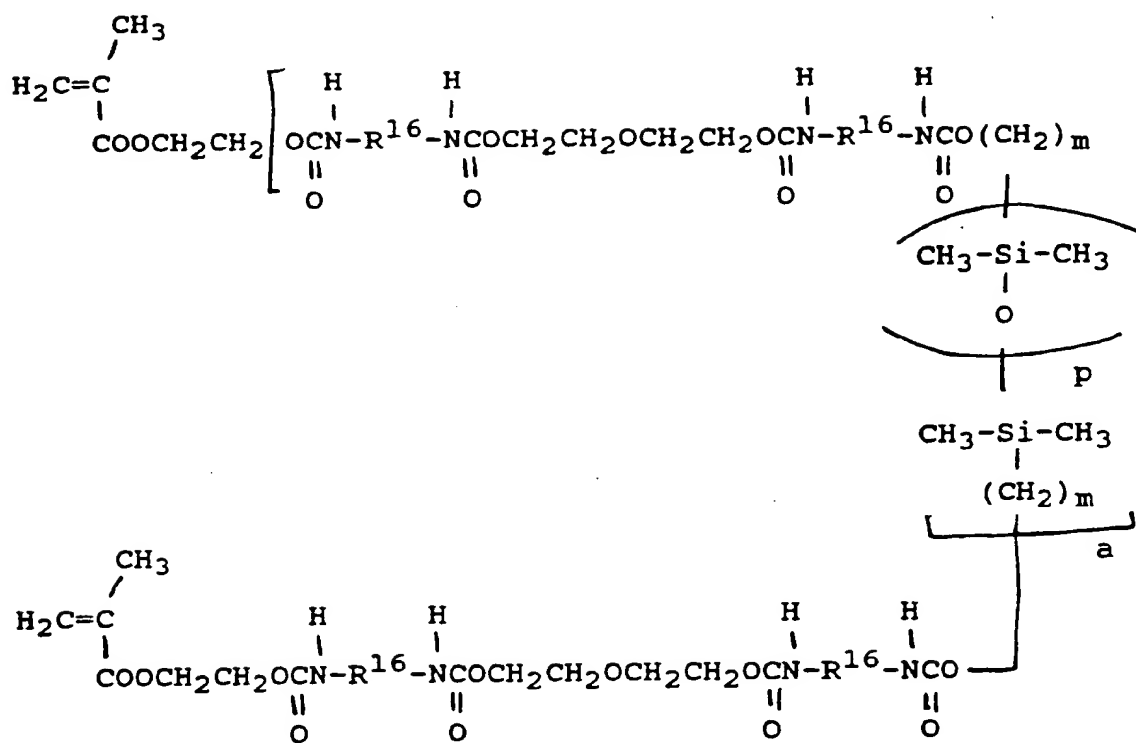
w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

z is 0 or 1.

12. The method of Claim 11 wherein said urethane-containing prepolymer is represented by formula:



wherein:

R^{16} is a diradical of a diisocyanate after removal of the isocyanate group and m , p and a are the same as previously defined.

13. The method of Claim 1 wherein said silicone-containing hydrogel composition comprises α, ω bis(methacryloxyalkyl) polysiloxane, N,N-dimethylacrylamide and N-vinyl pyrrolidone.

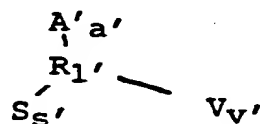
14. The method of Claim 1 wherein said silicone-containing hydrogel comprises a urethane-containing

prepolymer, N,N-dimethylacrylamide and N-vinyl pyrrolidone.

15. The method of Claim 1 wherein said silicone-containing hydrogel composition further comprises a relatively non-polar ring-containing compound selected from the group consisting of 2-vinyl-4,4-dimethyl-2-oxazolin-5-one, 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one, cyclohexane-spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) and 2-(1-propenyl)-4,4-dimethyl-oxazol-5-one.

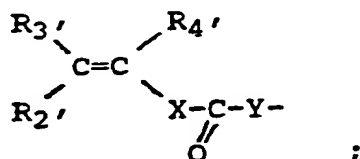
16. The method of Claim 1 wherein said silicone-containing hydrogel comprises an ethylenically terminated polysiloxane-containing monomer, N,N-dimethylacrylamide and N-vinyl pyrrolidone.

17. The method of Claim 1 wherein said silicone-containing hydrogel further comprises a crosslinking agent having the general schematic representation



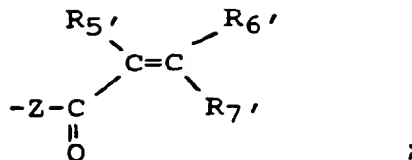
wherein

V denotes

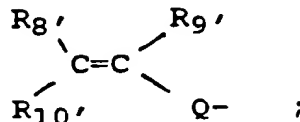


-35-

A' denotes



S denotes



R₁' is an alkyl radical derived from substituted and unsubstituted hydrocarbons, polyalkylene oxide, poly(perfluoro) alkylene oxide, dialkyl-capped polydimethylsiloxane, dialkyl-capped polydimethylsiloxane modified with fluoroalkyl or fluoroether groups;

R₂'-R₁₀' are independently H, or alkyl of 1 to 5 carbon atoms;

Q is an organic group containing aromatic moieties having 6 to 30 carbon atoms;

X, Y, and Z are independently O, NH or S;

v' is 1, or higher; and

a', s' are independently greater than or equal to 0, and a' + s' ≥ 1.

18. The method of Claim 17 wherein said crosslinking agent is methacryloxyethyl vinyl carbonate.

19. A silicone-containing hydrogel composition formed by curing a monomer mix comprising at least one acrylic-containing monomer, at least one vinyl-containing monomer and at least one silicone-containing prepolymer.

20. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is a urethane-containing prepolymer.

21. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is an ethylenically terminated polysiloxane-containing monomer.

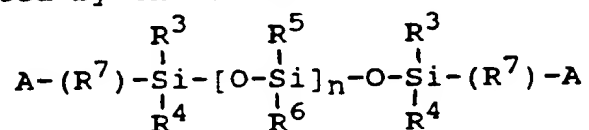
22. The hydrogel composition of Claim 19 wherein said vinyl-containing monomer may be selected from the group consisting of N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl acetamide, N-vinyl-N-methyl formamide, and N-vinyl formamide.

23. The hydrogel composition of Claim 19 wherein said vinyl-containing monomer is N-vinyl pyrrolidone.

24. The hydrogel composition of Claim 19 wherein said acrylic-containing monomer is selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol m thacrylate, 2-hydroxyethyl methacrylamid , diacetone acrylamide, methacrylic acid and acrylic acid.

25. The hydrogel composition of Claim 19 wherein said acrylic-containing monomer is N,N-dimethylacrylamide.

26. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is a poly(organosiloxane) prepolymer represented by the formula:



wherein:

A is an activated unsaturated group, such as an ester or amide of an acrylic or a methacrylic acid;

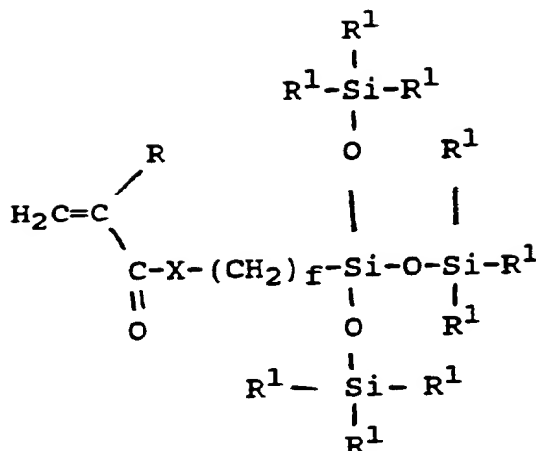
each R^3 - R^6 is independently selected from the group consisting of a monovalent hydrocarbon radical or a halogen substituted monovalent hydrocarbon radical having 1 to 18 carbon atoms which may have ether linkages between carbon atoms;

R^7 is a divalent hydrocarbon radical having from 1 to 22 carbon atoms;

and

n is 0 or an integer greater than or equal to 1.

27. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is a bulky polysiloxanylalkyl (meth)acrylic monomer having the formula:



wherein:

X is O or NR;

each R is independently hydrogen or methyl; and

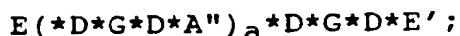
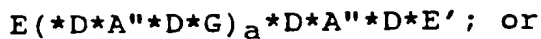
each R¹ is independently a lower alkyl or phenyl group; and

f is 1 or 3 to 10.

28. The hydrogel composition of Claim 27 wherein said bulky polysiloxanyalkyl (meth)acrylate is selected from the group consisting of methacryloxypropyl tris(trimethylsiloxy)silane, pentamethyldisiloxanylmethylmethacrylate, tris(trimethylsiloxy)methacryloxy propylsilane, phenyltetramethyldisiloxanylethyl acetate, and methyldi(trimethylsiloxy)methacryloxymethyl silane.

29. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is a urethane-containing

prepolymer having the following schematic representations:



wherein

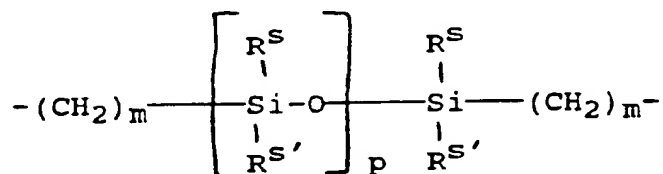
D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aryl diradical or an alkylaryl diradical having 1 to 40 carbon atoms and which may contain ether, thio or amine linkages in the main chain;

* denotes a urethane or ureido linkage;

a is at least 1;

A'' denotes a divalent polymeric radical of formula:

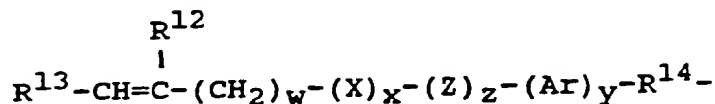


wherein: R^S and $R^{S'}$ independently denote an alkyl or fluoro-substituted alkyl group having 1 to 10 carbon atoms which may contain ether linkages between carbon atoms;

m is at least 1; and

p provides a moiety weight of 400 to 10,000; -

E and E' independently denote a polymerizable unsaturated organic radical represented by formula:



wherein: R^{14} denotes a divalent alkylene radical having 1 to 10 carbon atoms;

R^{12} denotes H or CH_3 ;

R^{13} denotes H, a (C_1 - C_6) alkyl radical or a $-CO-Y-R^{15}$ group wherein Y is $-O-$, $-S-$ or $-NH-$ and R^{15} is a alkyl radical having 1 to 12 carbon atoms;

X is $-CO-$ or $-OCO-$;

Z is $-O-$ or $-NH-$;

Ar denotes an aromatic radical having 6 to 30 carbon atoms;

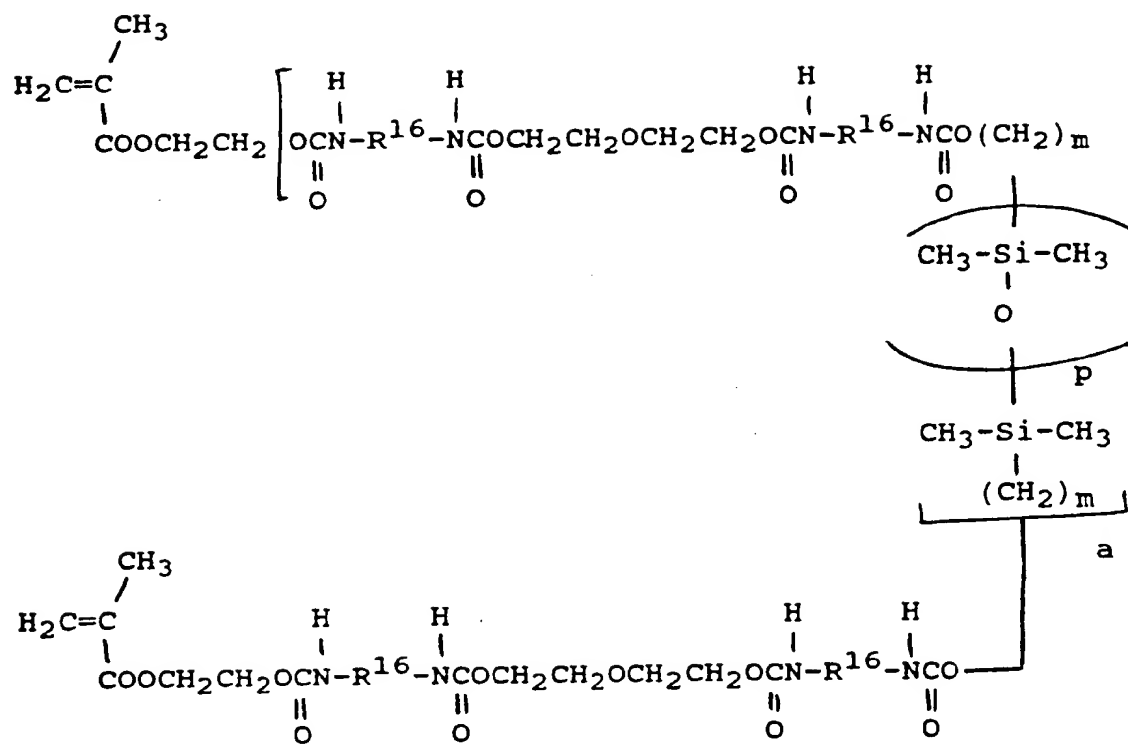
w is 0 to 6;

x is 0 or 1;

y is 0 or 1; and

z is 0 or 1.

30. The hydrogel composition of Claim 29 wherein said urethane-containing prepolymer is represented by the formula:



wherein:

R^{16} is a diradical of a diisocyanate after removal of the isocyanate group and m, p and a are the same as previously defined.

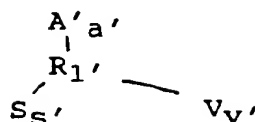
31. The hydrogel composition of Claim 22 wherein said silicone-containing prepolymer is α,ω bis(methacryloxyalkyl) polysiloxane, said acrylic-containing hydrophilic wetting monomer is N,N-dimethylacrylamide and said vinyl-containing hydrophilic wetting monomer is N-vinyl pyrrolidone.

32. The hydrogel composition of Claim 19 wherein said silicone-containing prepolymer is a urethane-containing prepolymer, said acrylic-containing monomer is N,N-dimethylacrylamide and said vinyl-containing monomer is N-vinyl pyrrolidone.

33. The hydrogel composition Claim 19 wherein said silicone-containing hydrogel composition further comprises a relatively non-polar ring-containing compound is selected from the group consisting of 2-vinyl-4,4-dimethyl-2-oxazolin-5-one, 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one, cyclohexane-spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) and 2-(1-propenyl)-4,4-dimethyl-oxazol-5-one.

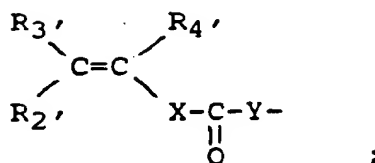
34. The hydrogel composition of Claim 19 wherein said silicone-containing hydrogel composition is an ethylenically terminated polysiloxane-containing monomer said acrylic-containing hydrophilic wetting monomer is N,N-dimethylacrylamide and said vinyl-containing hydrophilic wetting monomer is N-vinyl pyrrolidone.

35. The hydrogel composition of Claim 19 wherein said silicone-containing hydrogel further comprises a crosslinking agent having the general schematic representation:

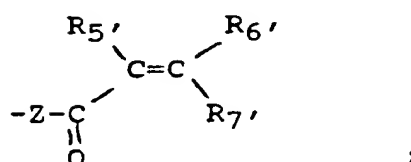


wherein

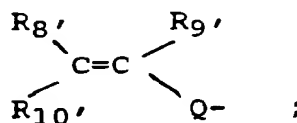
V denotes



A' denotes



S denotes



R_1' is an alkyl radical derived from substituted and unsubstituted hydrocarbons, polyalkylene oxide, poly(perfluoro) alkylene oxide, dialkyl-capped polydimethylsiloxane, dialkyl-capped polydimethylsiloxane modified with fluoroalkyl or fluoroether groups;

$R_2', -R_{10}'$ are independently H, or alkyl of 1 to 5 carbon atoms;

Q is an organic group containing aromatic moieties having 6 to 30 carbon atoms;

X, Y, and Z are independently O, NH or S;

v' is 1, or higher; and

a' , s' are independently greater than or equal to 0, and $a' + s' \geq 1$.

36. The hydrogel composition of Claim 35 wherein said crosslinking agent is methacryloxyethyl vinyl carbonate.

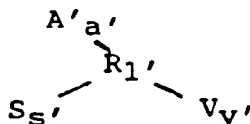
37. A biomedical device made from the hydrogel composition of Claim 19.

38. A contact lens made from the hydrogel composition of Claim 19.

39. The contact lens of Claim 38 wherein said hydrogel composition comprises α,ω bis(methacryloxybutyl) polysiloxane, N,N-dimethylacrylamide and N-vinyl pyrrolidone.

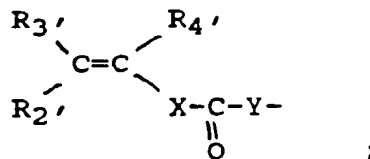
40. The contact lens of Claim 38 wherein said hydrogel composition further comprises a relatively non-polar ring-containing compound is selected from the group consisting of 2-vinyl-4,4-dimethyl-2-oxazolin-5-one, 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one, cyclohexane-spiro-4'-(2'-isopropenyl-2'-oxazol-5'-one), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) and 2-(1-propenyl)-4,4-dimethyl-oxazol-5-one.

41. The contact lens of Claim 38 wherein said hydrogel composition further comprises a crosslinking agent having the general schematic representation

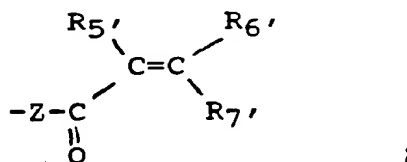


wherein

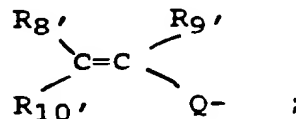
V denotes



A' denotes



S denotes



R_1' is an alkyl radical derived from substituted and unsubstituted hydrocarbons, polyalkylene oxide, poly(perfluoro) alkylene oxide, dialkyl-capped polydimethylsiloxane, dialkyl-capped polydimethylsiloxane modified with fluoroalkyl or fluoroether groups;

R_2' , R_{10}' are independently H, or alkyl of 1 to 5 carbon atoms;

Q is an organic group containing aromatic moieties having 6 to 30 carbon atoms;

X, Y, and Z are independently O, NH or S;

v' is 1, or higher; and

a', s' are independently greater than or equal to

0, and $a' + s' \geq 1$.

42. The contact lens of Claim 41 wherein said crosslinking agent is methacryloxyethyl vinyl carbonate.

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FIG. 1

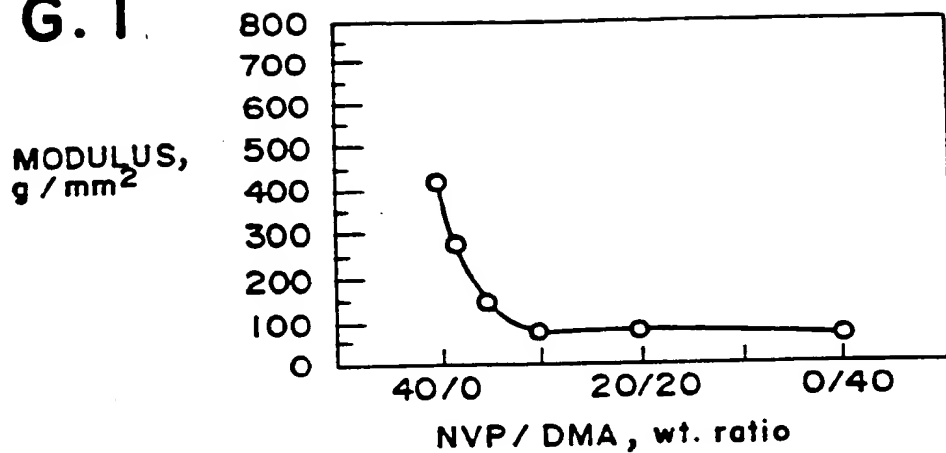


FIG. 2

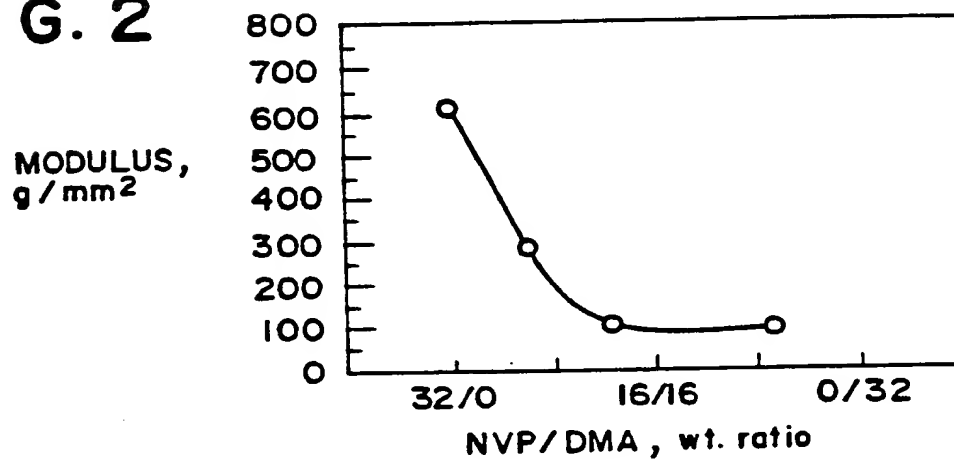
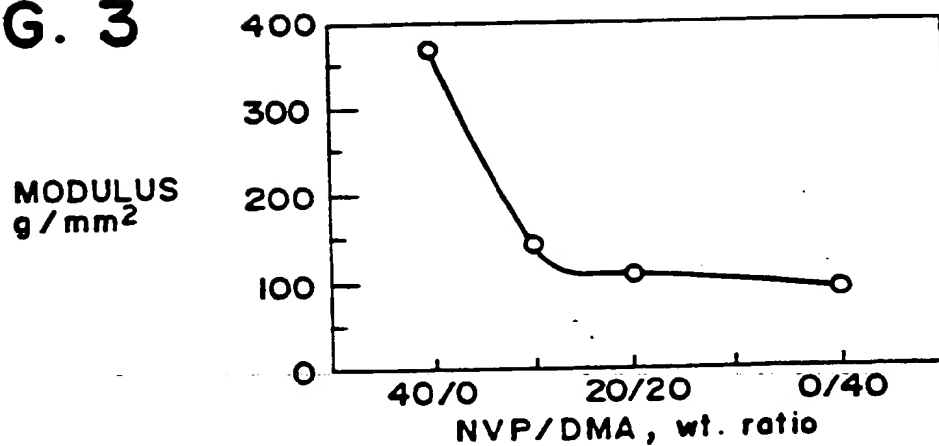


FIG. 3



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/09538

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F299/04; C08F299/08; G02B1/04; C08F299/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; G02B	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 343 927 (CHANG) 10 August 1982 see examples 4-9,25,26 ---	1,3, 5-10,16, 19,21, 23-25, 27,28, 34,37,38
X	FR,A,2 398 084 (CIBA-GEIGY) 16 February 1979 see page 6, line 32 - page 7, line 38; examples 4,7,14,17,18 --- -/-	1-3,5,6, 8,10,11, 19-21, 23,24, 26,28, 29,37
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23 MARCH 1993	19. 04. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MEULEMANS R.A.M.	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP, A, 0 080 539 (TSUETAKI) 8 June 1983 see examples 5, 8, 12, 13, 19 -----	1, 3, 5, 6, 19, 23, 24, 37, 38
X	EP, A, 0 338 656 (BAUSCH & LOMB INCORPORATED) 25 October 1989 -----	1, 3, 15, 19, 21, 33, 37, 38

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9209538
SA 66935

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4343927	10-08-82	US-A- 4182822	08-01-80
		AT-T- 5260	15-11-83
		CA-A- 1118938	23-02-82
		EP-A,B 0016138	01-10-80
		WO-A- 8000253	21-02-80
FR-A-2398084	16-02-79	US-A- 4136250	23-01-79
		DE-A,C 2831274	08-02-79
		GB-A,B 2002788	28-02-79
		JP-C- 1430546	24-03-88
		JP-A- 54022487	20-02-79
EP-A-0080539	08-06-83	JP-B- 62036046	05-08-87
		None	
EP-A-0338656	25-10-89	US-A- 4810764	07-03-89
		JP-A- 1308419	13-12-89

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82